Methods for Preparation of Absorbent Microspherical Tannin Resin

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SYNOPSIS

Tannin beads formed by reaction of Mimosa tannin (condensed-type tannin) with form-aldehyde in nonpolar polybutenous medium were microspherical resins. Resins prepared with 37.5% tannin concentration were porous spherical resins with 139.22 m^2/g of surface area (adsorption method of iodine in n-hexane, 2.1 m^2/g for the dried beads by the Brau-nauer-Emett-Teller (BET) method) and were strong enough to withstand use on a column. The spherical resin adsorbed 3.7 mmol of Cr^{6+} ions per one gram dry weight of resin (by batch method), this adsorption being comparable to commercial adsorbent.

INTRODUCTION

The principal use of the so-called condensation-type tannins, represented by Mimosa (Wattle, Acacia sp.) and Quebracho tannin, is as a tanning agent in the leather industry. Another use is as a raw material in the manufacture of adhesives. The phenolic hy-droxy groups of these condensation type tannins are linked by an ion bond, a quinone bond, and/or a hydrogen bond to the protein and alkaloid.[1,2] In ad-dition, these condensation-type tannins can adsorb certain heavy-metal ions.[3] In order to utilize this adsorption property tannins from bark[4,5] or green tea[6] were crosslinked by formaldehyde. However, using tannins immobilized at the concentration at which they are found in nature, adsorption is limited. In this report, a method of preparation of fine, po-rous, spherical resin by reaction of tannin with formaldehyde is described and the use of this ma-terial on a column is considered.

EXPERIMENT

Materials and Reagents

The raw material was Mimosa tannin (MT). A 20% aqueous solution of the commercial tannin (powder)

was centrifuged (at 3000 rpm for 30 min) to remove insoluble constituents and then freeze-dried. The properties of MT are shown in Table I. Formalin (37% solution of formaldehyde in water) was used as formaldehyde solution (Wako Pure Chemical In-dustries Co.). The fine, spherical resin was prepared from polybutene (technical grade). Toluene and methanol used for washing of the granulated spher-ical resin were analytical-grade reagents used with-out further purification.

Methods

Viscosity Measurements and Gel-Point Determination

Aqueous solutions of MT were warmed at the pre-scribed temperature and mixed rapidly after addition of prewarmed formaldehyde solution. Viscosity was measured at intervals using a B-type viscometer. Gel point was defined as the time at which the sample no longer adhered to the rod of the viscometer above 10,000 cP. Viscosities of the polybutene used in the preparation of the resin were measured with the B-type viscometer in a thermostated water bath.

Gel Preparation

Fine, spherical resins were prepared as follows: 1.5–1.7 L of polybutene of the desired viscosity was placed in 2-L flasks, warmed to the desired temper-

Table I   Composition of Mimosa Tannin

Tannin[a]	Precipitate by HCl–HCHO (%)	Equivalent molecular weight	Ash (%)
74.1	89.4	170	1.3

[a] Determined by colloidal titration method.

ature, and stirred at the prescribed rpm in a thermostatically controlled water bath. MT (molecular weight defined as 270) and formaldehyde were mixed at the desired molar ratio. Deionized water was added to give the desired final concentration of MT. The solution of MT and formaldehyde was added to the warm polybutene under controlled conditions of agitation and temperature. The resulting MT–HCHO resin was harvested by filtration, washed five times in toluene, and then refiltered and washed five times in methyl alcohol. In some experiments the resins were also washed in 1.2N HCl followed by several washes in deionized water.

Characters of the Spherical Resins

Grain size distributions were measured by sieving of vacuum-dried (at 60°C) resins through standard screens. The specific surface area of wet beads was measured by the iodine adsorption method.[7,8] The iodine adsorption method used was as follows: the water in the spherical resin prepared from 37.5% MT was replaced with the dried methanol, and the alcohol was replaced with the dried hexane, and then adsorbed the iodine from the iodine–hexane solution (in a batch operation for 96 h). The adsorption isotherms were obtained by the titration of the residual iodine with sodium thiosulfate. The specific surface area was evaluated by the 21.1 $Å^2$ as the area of one molecular of iodine[8] to the measured maximum amount of the adsorbed iodine. The specific surface area of dry beads was measured by the BET method using an automated system (Shimazu seisakusho, type-2200).

Topography of Air-dried Spherical Resin

The surface of the spherical resin and the divided face of broken resin were observed in a scanning electron microscope (Nihon denshi, type JSM-35).

Other Characteristics of Beads

Bed volume changes were calculated by measurement of changes in resin layer heights (the initial height of the resin layer was 500 mm) in the 19.2 × 550 mm column equilibrated with deionized water (1.0 cP) or aqueous glycerin solution (14 cP).

Contractions in resin volume caused by aqueous salt solutions were measured as follows: Resins were first equilibrated in deionized water and the volume measured in a 50-mL measuring cylinder. The same resins were equilibrated successively in NaCl solutions of increasing concentration and the volumes measured. Finally, the resins were equilibrated again in deionized water and the volumes measured. The resins were vacuum-dried at 60°C and weighed.

Contraction of Resin upon Drying

The volume of resin equilibrated with deionized water was measured. After filtration with a glass filter (1G3) and vacuum drying at room temperature, the weight and volume of the resin were measured. This resin was then hydrated in deionized water, and the parameters of the restored resin were measured.

The adsorption properties of the tannin resin were measured using Cr^{6+} ions. Cr^{6+} ions at 205 ppm in 100 mL acetic acid buffer solution (pH 4) were adsorbed by wet resin (0.05 g dry weight) at 23°C for 96 h stirring at 50 rpm in a 360 somersault-type stirrer. The concentrations of residual Cr^{6+} ions were measured by atomic absorption spectrophotometry (Nihon jarlel ash Co. Ltd., AA-500), and the amount of the adsorbed Cr^{6+} ions calculated.

RESULTS AND DISCUSSION

Viscosity of Aqueous MT Solutions

The composition of commercial tannin extracted with water was 70% phenolic tannin and 20–25% nontannin,[9] the latter comprising monosaccharides and polysaccharides. The tannin constituent is mainly the flavonoid skeleton, 70% of which has a resorcinol A-ring and a pyrogallol B-ring and 25% of which has a resorcinol A-ring and a catechol B-ring. The remaining 5% has a phloroglucinol-type A-ring.[9] The molecular weight of MT to which 10–11 units of the flavonoid can bind is not more than 30,000, and the number-average molecular weight is 1250.[9] In another report, the molecular weight, measured by the cryoscopic method, was 790–2280, and it appears that 85% of the material has a molecular weight of 1260 to 2280.[10] It follows therefore that an aqueous solution of MT is highly viscous. The relation between viscosity, concentration, and temperature of aqueous MT solutions is shown in Figure 1. The lower the concentration of MT, the
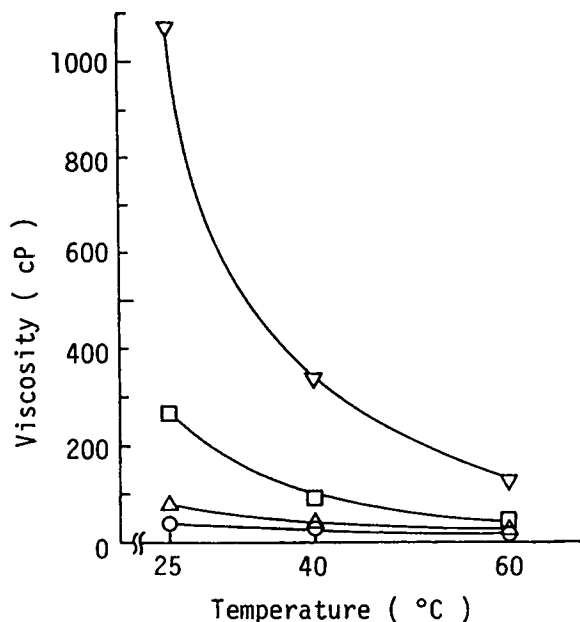

Figure 1 Temperature dependence of the MT viscosity: (O) 30% MT, (△) 35% MT, (□) 40% MT, (▽) 50% MT.

with stirring, and the viscosity was measured at various times. Initial viscosities were lower than 60 cP and were similar to those recorded with 35–40% aqueous MT solutions without formaldehyde (Fig. 1). Figure 2 shows that the more formaldehyde added, the shorter the gelation time. The gel with a molar ratio of 0.5 (HCHO:MT) had a gel time of about 200 min, and the resulting resin was soft and weak. It seemed therefore that this tannin resin would need to be heated to 60°C for an additional period or possibly subjected to other heat treatment so that it could be used in a column. In contrast, the resin derived from a molar ratio 1.0 formed a hard, strong resin that should be suitable for use in a column after the same heat treatment (60°C for 200 min). The influence of temperature on the gelation time of a 37.5% MT solution mixed with HCHO at a molar ratio of 1:1 is shown in Figure 3. A gel did not form at 40°C. At 60°C a gel formed after 130 min. When the solution was heated for 200 min, the strength of the resin obtained was sufficient for use in a column. The time for the preparation of the spherical resin was shorter at 70 and 80°C than at 60°C. Since the purpose of granulation is to produce an adsorption resin, it is considered that a resin with a greater specific surface area (macro-
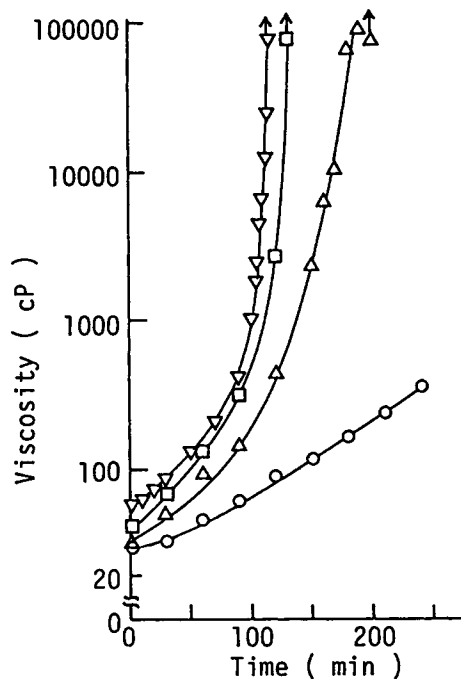
lower the effect of temperature on viscosity such that the viscosity of a 30% MT solution was not changed appreciably by changes in temperature from 25 to 60°C. In contrast, the viscosity of a 50% MT solution was reduced by a factor of 8.3 over the same temperature range and that of a 40% solution, by a factor of 6.3. These results suggest that if the MT solution is heated to about 60°C, viscosity is not a factor that needs to be considered during resin preparation.

Gelation Time

MT reacts with HCHO at the 6- and 8-positions. Or, if the 6- or 8-positions on the A-ring of the flavonoid skeleton are methylolated around neutrality, then it is considered that polymerization of MT occurs by the formation of methylene bridges between the flavonoid units.[9] Because the tannin formaldehyde resins in this study were made by reaction of MT with formaldehyde in the absence of a catalyst and the pH during resin preparation was about 4.5, it was considered that the reaction of MT with formaldehyde occurred at the 6- and 8-positions of the flavonoid skeleton. The effect of different molar ratios of HCHO to flavonoid skeletons on viscosity changes up to gelation are shown in Figure 2. The final concentration of MT was adjusted to 37.5% by the addition of deionized water and the solution was heated to 60°C. Formaldehyde at 60°C was added

Figure 2 Effect of the molar ratio between HCHO and MT on the gelation time: concentration of the MT solution, 37.5%; temperature, 60°C. (O) molar ratio 0.2, (△) molar ratio 0.5, (□) molar ratio 1.0, (▽) molar ratio 2.0.
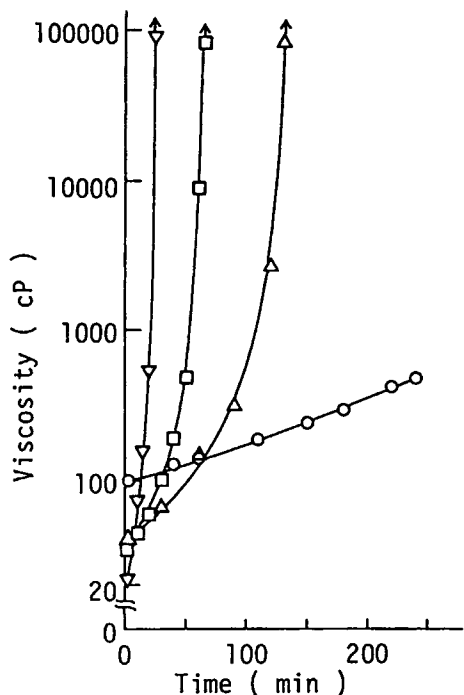
Figure 3 Effect of temperature on the gelation time: molar ratio between HCHO and MT, 1.0; concentration of MT solution, 37.5%. (○) 40°C, (△) 60°C, (□) 70°C, (▽) 80°C.
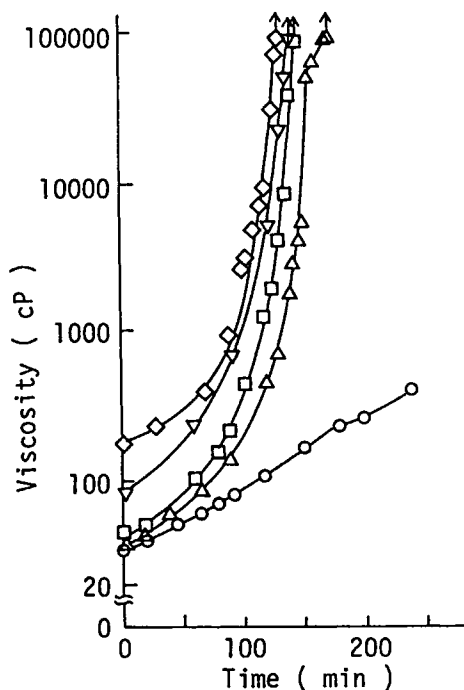
reticular type resin), should enhance adsorption capacity. Since MT in aqueous solution reacts with HCHO and polymerizes, such a macronetwork structure could possibly be achieved by increasing the quantity of the water.

In view of this the effect on viscosity of different concentrations of MT aqueous solution was studied (Fig. 4). A 30% solution of MT did not gel during the experiment, and whereas 35% MT solution did gel, some of the prepared spherical resin disintegrated during the washing process. However, resins prepared from more concentrated MT solutions (≥ 37.5%) were stronger. The higher the concentration of MT, the more rigid and more deeply colored the resin obtained. However, it was considered that the degree of the macronetwork structure decreased with increasing MT concentration.

Effect of Viscosity of Medium and Rate of Stirring on Resin Grain Size Distribution

Given the preparative procedure used in this study, it is thought that the grain size of the dispersed spherules was dependent on the viscosity of the me-
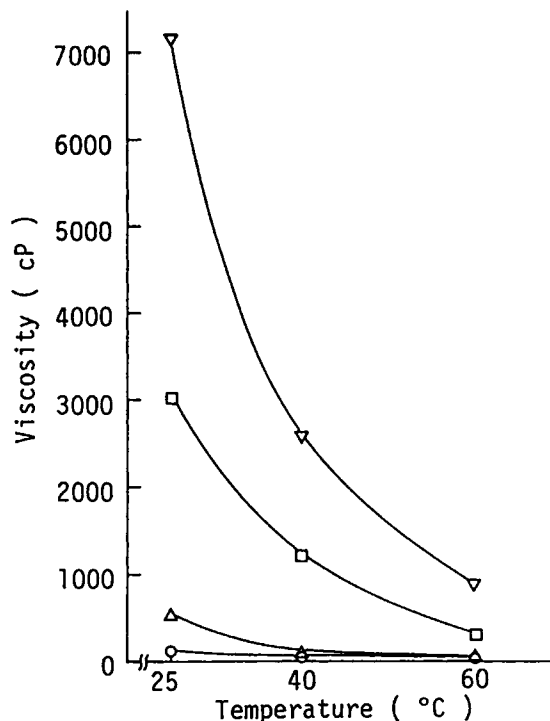

Figure 4 Effect of the concentration of MT solution on the gelation time: temperature, 60°C; molar ratio HCHO and MT, 1.0. (○) 30.0% MT, (△) 35.0% MT, (□) 37.5% MT, (▽) 40.0% MT, (◇) 42.5% MT.

Figure 5 Temperature dependence of polybutene viscosity: (○) number-average molecular weight 370, (△) number-average molecular weight 430, (□) number-average molecular weight 580, (▽) number-average molecular weight 720.

Table II   Relationship between the Preparation Conditions of the Spherical Resin and the Distribution of the Grain Size

Stirrer Speed (rpm)	Viscosity of the Medium[a] (cP)	Bulk Density		Distribution of Grain Size[d] (%)		
		Dry (g)/Wet[b] (mL)	Wet[c] (g)/Wet (mL)	~16 Mesh	16–42 Mesh	42~ Mesh
200	32.5	—	—	92.6[e]	7.4	0.0
	54	0.24	0.75	35.2[e]	62.8	2.0
	325	0.23	0.71	0.0	83.8	16.2
	880	0.20	0.74	0.0	0.0	100.0
250	54	0.21	—	8.7	76.3	15.0
300	54	0.21	0.73	1.3	92.9	5.8
350	32.5	0.25	0.71	0.7	86.5	12.8
	54	0.17	0.65	0.0	73.1	26.9
500	32.5	0.22	—	0.1	97.2	2.7
	54	0.26	0.74	0.0	54.6	45.6
	325	0.21	0.61	0.0	0.0	100.0
	880	0.23	0.71	0.0	0.0	100.0

[a] Viscosity at 60°C.
[b] Volume of the resin in water.
[c] Weight of the wet resin after centrifugation for 5 min at 3000 rpm.
[d] Vacuum-dried at 60°C, and then sieved.
[e] The value including nonspherical resin.
Other conditions for the resin preparation: Concentration of MT solution, 37.5%; molar ratio between HCHO and MT, 1.0; temperature, 60°C.

dium, the viscosity of the raw material, and the rate of stirring. The minimum concentration of MT required to increase the specific surface area of the prepared fine spherical resin was 35%, estimated by considering the strength of the prepared resin. When

the spherules were prepared at temperatures over 60°C, the MT gelled and at higher temperature, gelation was faster. Therefore, if the spherical resins
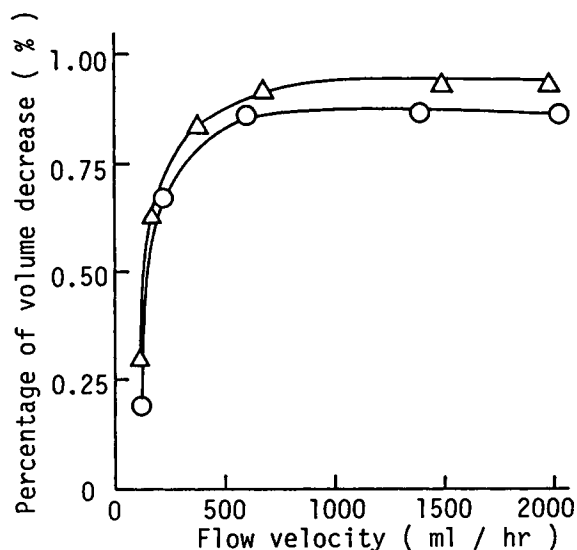

Figure 6   The decrease in bed volume of a spherical resin column: (O) The water was made to flow through the column. (△) The spherical resin was preequilibrated with aqueous glycerin solution (14 cP) and then glycerin solution was made to flow through the column.
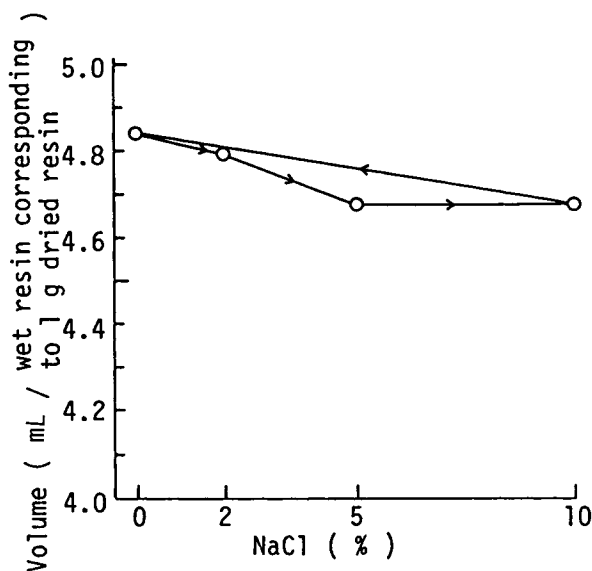

Figure 7   Effect of the concentration of NaCl on the volume changes of the spherical tannin resin in water. The resins were equilibrated with each concentration of NaCl aqueous solution for 2 days at room temperature. Condition for the preparation of the resin: MT–HCHO = 1:1. The concentration of MT when prepared the spherical resin was 37.5%; 60°C; 300 rpm; 200 min.

were prepared at 60°C with 35% MT aqueous so-
lution, the viscosity of the MT solution was about
35 cP, as shown in Figure 1. In order to disperse
such highly viscid materials in the medium at a cer-
tain rate of stirring, the viscosity of the medium
must be similar to or more viscous than the MT
solution at 60°C, and both materials must be insol-
uble in each other. The viscosities of polybutenes
with different number-average molecular weights are
shown in Figure 5. Polybutene satisfies these con-
ditions, and it is considered that polybutenes with
number-average molecular weights of 370 (32.5 cP)
or 430 (54 cP) were optimal. The effects of the po-
lybutene and the rate of stirring on grain size dis-
tribution of the spherical resin prepared with 37.5%
MT at 60°C are shown in Table II. The spherical
resin was prepared as follows: 1.5 L of polybutene
were added to a 2-L separable flask. The T-shaped

stirring rod had two shuttlecocks (3.5 cm long × 1.6
cm wide × 2 mm thick) and was set 1 cm above the
base of the flask. The results were as follows: If the
lowest viscosity polybutene (32.5 cP, at 60°C) was
used as the medium at stirring speeds of 200 rpm,
it seems probable that the MT solution did not dis-
perse satisfactorily because substantially all the
product was retained by a 16-mesh sieve. Moreover,
the products formed a conglomerate and not a
spherical resin. However, when stirred at 500 rpm,
the majority of the product was a spherical resin
within the range of 16 and 42 mesh found with other
viscosities of polybutene in various preparation
conditions. This distribution of grain size is similar
to the range of 10–48 mesh for general chelating or
ion exchange resins. When more viscous polybutene
was used, the optimal rate of stirring appeared to
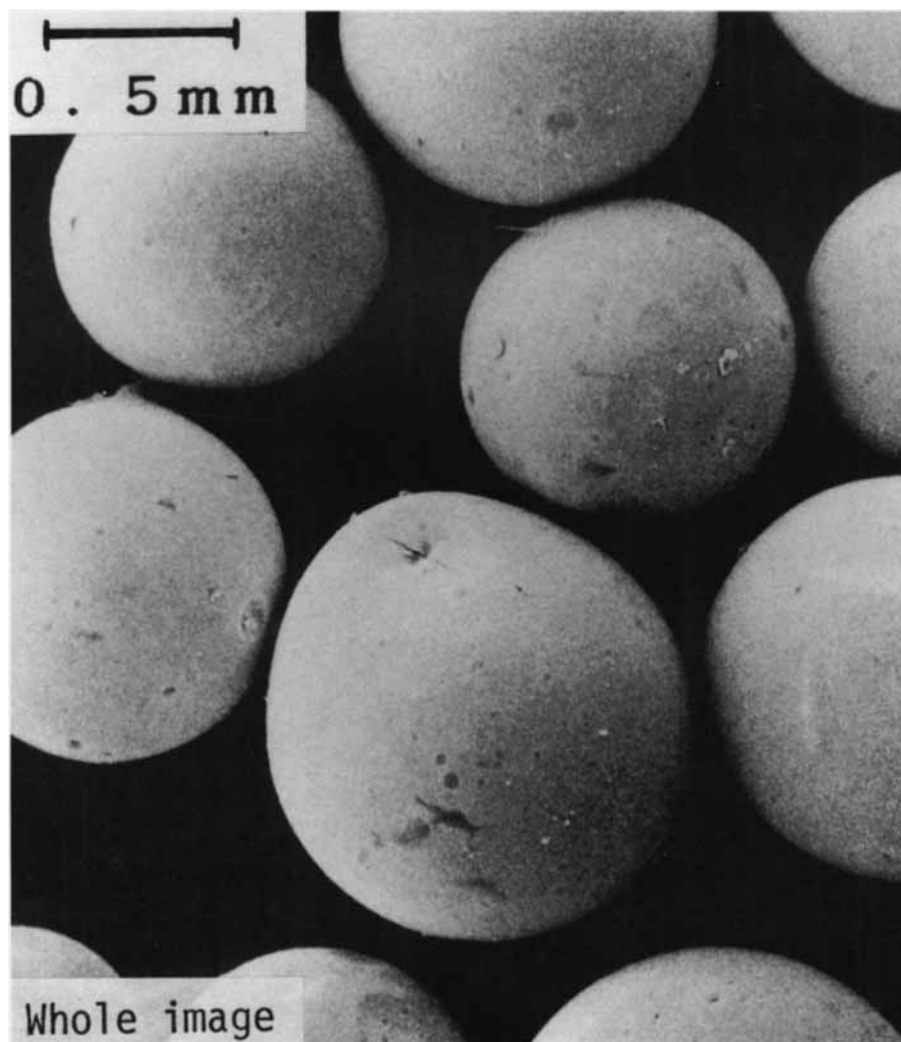decrease. For example, the optimum rate of stirring

Plate 1   Whole image of the spherical resin.

was 300 rpm with the 54 cP of polybutene. In the case of very viscous polybutene (880 cP), even with the slower rate of stirring (200 rpm), spherical resin was prepared, the grain size of which was smaller than the 42 mesh.

Properties of the Spherical Resin

It is preferable if adsorbent spherical resins can be used in column-based as well as batch-based methods. A problem that arises in column-based methods is the compression of the resin caused by the viscosity of the liquid following through the column. The spherical resins made using a molar ratio of 1.0 with a stirring rate 300 rpm at 60°C were charged to a height of 550 mm in a 19.2 × 630 mm column, after prior equilibration in deionized water (3.5 cP) or in the aqueous glycerin solution (14 cP). Then

deionized water or aqueous glycerine solution were passed through the column and the resulting decrease in bed volume was measured (Fig. 6). Bed volume decreased rapidly with flow rates up to 600 mL/h with both deionized water and aqueous glycerin solution. No further decrease was observed as higher flow rates and the maximum effect was less than 1%. Furthermore, this spherical resin did not reduce the flow rate by compression, and its strength was satisfactory for use in columns. When the spherical tannin resins were equilibrated in various concentration aqueous NaCl solution and in water, the change quantities in volume of the spherical tannin resin were shown in Figure 7. The volume of the wet spherical tannin resin, corresponding to 1 g of dry resin, was 4.48 mL when equilibrated in distilled water. When equilibrated in 5% aqueous NaCl
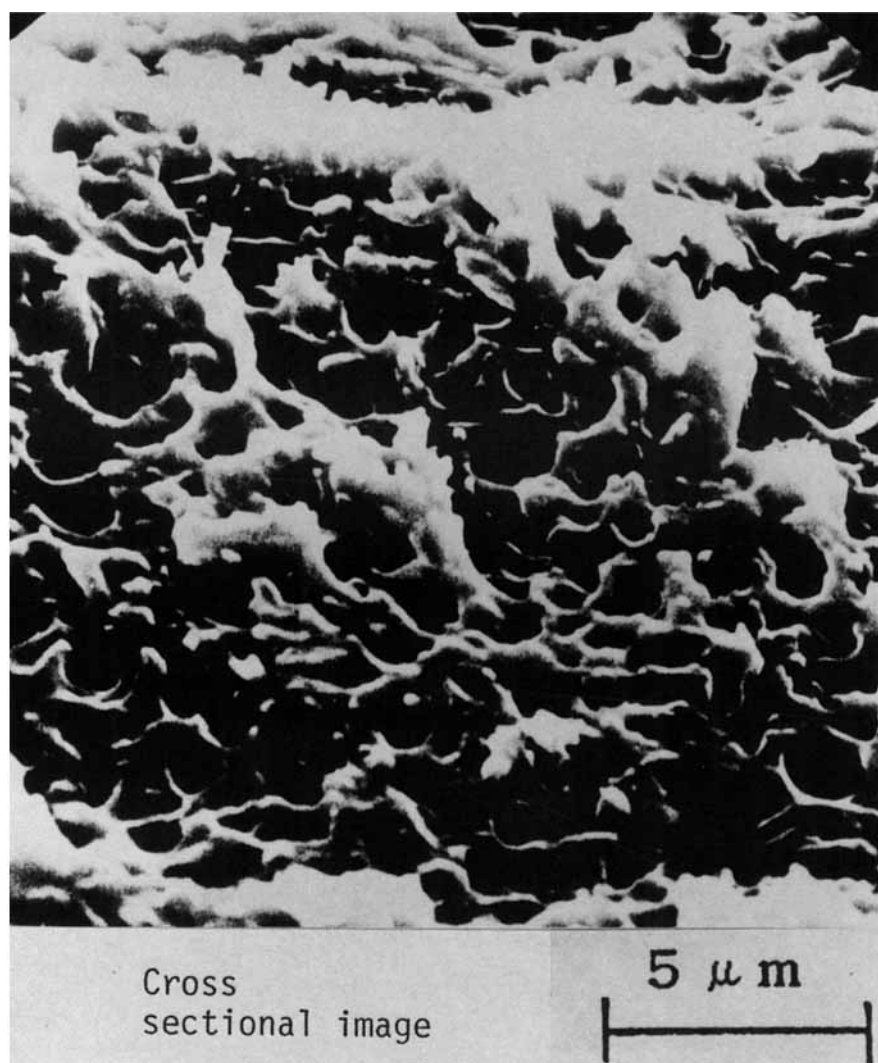

Plate 2   Cross-sectional image of the spherical resin.

aqueous solution, the volume was 4.68 mL, 3.41% of the initial volume decrease. No further decrease in volume was seen even in 10% NaCl. It was thought that this decrease in volume was responsible for the lixiviation of water in the resin by the difference in NaCl concentration. Changes in the structure of the resin were not thought to have occurred (other than this concentration effect) because the volume of the spherical resin soaked in 10% NaCl was restored by equilibration in deionized water. The volume of the wet resin contracted from 100 to 27.33 mL by vacuum drying at room temperature. This dried resin was restored only 72.67 mL after rehydration in deionized water. Based on this result, dried resin was thought to be inferior to undried resins in their adsorbent capabilities. Regarding the adsorption of Cr^{6+} ions, one gram of resin adsorbed 3.7 mmol of Cr^{6+} ions in preliminary experiments. There is not great difference between this amount of the adsorbed Cr^{6+} ions and the amount of the adsorbed Cr^{6+} ions by commercial resin as an adsorbent of Cr^{6+} ions.

Scanning Electron Microscopy and Calculation of Surface Area of the Spherical Resin

The whole image of the spherical resin is shown in Plate 1, and the cross-sectional image of the resin is shown in Plate 2. It can be seen that prepared resins were approximately spherical and that the internal structures were open networks. The specific surface area of the fine spherical resin prepared from 37.5% MT at a molar ratio of 1.0 at 60°C was 139.22 m^2/g by the iodine adsorption method from n-hexane–iodine solution and 2.1 m^2/g by the BET method for the air-dried resin. It appears therefore that undried resin had a high specific surface area and was suitably porous for use as an adsorbent.

CONCLUSIONS

Methods for preparation of spherical adsorption resins from the reaction of condensed-type tannin (MT) with HCHO were studied and the following results obtained:

1. Spherical tannin resins could be prepared easily by the reaction of MT with HCHO with stirring and heating in polybutene.
2. It could be seen by scanning electron microscopy that the prepared spherical tannin resin is approximately spherical, porous, and has an internal network structure.
3. These resins were slightly contracted in aqueous salt solutions above 5%. However, this resin was found to withstand use in a column. Loss of bed volume was less than 1% due to compression when glycerin solution (14 cP) flowed through the column.
4. In a preliminary experiment wet resin containing one gram dry weight of resin adsorbed 3.7 mmol of Cr^{6+} ions. Cr^{6+} ion adsorption of this resin was comparable to that of commercial chelating resin. [i.e., with Cr^{6+} ion at 500 ppm, 100 mL of commercial resin (density 0.73, $-SO_4$ type resin), column method and space velocity (SV) 10,[11] one gram of commercial resin adsorbed 3 mmol of Cr^{6+} ions.]

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